PATENT SPECIFICATION

(11) **1 535 481**

(54) REMOVAL OF ORGANIC COMPOUNDS FROM AQUEOUS LIQUIDS BY SOLVENT EXTRACTION

(71)   We, INSTITUT FRANCAIS DU PETROLE, a body corporate organised and existing under the laws of France, of 4 avenue de Bois-Preau, 92502 Rueil-Malmaison Cedex, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

The present invention concerns the removal or extraction of hydrocarbons or other organic compounds from aqueous liquids in which they are present either in a dissolved state or as emulsions (dispersions).

The process described below has been found particularly useful for the treatment of aqueous liquids used for washing hydrocarbon materials and waste aqueous liquids discharged from industrial units, which carry pollutant hydrocarbons, or other organic pollutants, and which, according to standard or mandatory precautions against pollution, cannot be directly discarded into the environment, or cannot be re-used without being purified.

These aqueous liquids contain organic materials, in small proportion, often as traces.

In the case of hydrocarbon-contaminated water, for example, the aqueous solutions are often highly dilute. Hydrocarbons such as, for example, ethylbenzene and styrene, have in fact respective solubilities in water close to 0.015% and 0.033% by weight, at room temperature. The amounts of emulsified hydrocarbons which may be encountered are slightly higher, but scarcely exceed 5% by volume.

Frequently, it also happens that waters are polluted by small amounts of malodorous or toxic organic materials (e.g. phenols and chlorophenols) which need to be removed.

The usual extraction techniques (for example distillation, liquid-liquid extraction, stripping) cannot be used at low cost in the case of very dilute solutions. They would require economically useless and costly investment, high power consumption and, additionally, such arrangements would not always be capable of solving the purification problems posed by the presence of the liquids to be decontaminated.

According to the invention there is provided a process for extracting an organic compound from an aqueous liquid containing it, that comprises contacting the aqueous liquid containing the organic compound with an extraction mass comprising particles of an inert porous solid carrier having a grain porosity of at least 0.1 and containing an immobilized organic solvent, with substantially no organic solvent in the space between the particles, said solvent being a good solvent for the organic compound to be extracted and having low solubility in the aqueous liquid, said organic solvent and porous carrier being such that the solvent is chemically inert with respect to the carrier and has substantially no swellinv effect on the carrier; the process also comprising regenerating the extraction mass after said contact by contacting it with an organic solvent as hereinabove defined.

The process has been found to be operable with a low solvent consumption, owing to the use of an extraction technique capable of greater efficiency than the conventional liquid-liquid extraction.

Another advantage in practice is that stirring of the medium, usually required for efficient contact, is unnecessary. The risk of forming stable emulsions between water and organic materials is thus avoided. Moreover, it has been observed that passage of contaminated aqueous liquid over the impregnated carrier, during performance of a process according to the invention, can result in breaking of any already-existing stable

emulsions of organic materials in water, although they may withstand extended decantation.

5 The present process also allows use of an easily regenerable extraction agent. The working of such an extraction agent seems to be basically as follows:

The organic materials present in water are supposed to dissolve in an appropriate organic liquid (called solvent), confined in
10 the pores of a porous solid used as carrier.

The solvent used in the process of the invention preferably has the following properties:

15 its solubility in aqueous liquid is desirably smaller than 0.1% by weight and preferably smaller than 0.01% by weight. It is preferably lower than the solubility in the same aqueous liquid of the organic compound to
20 be extracted, preferably at least three times lower;

it is preferably a good solvent for the organic material to be extracted, i.e. the distribution coefficient of this organic material
25 (ratio of the respective concentrations of the organic material in the solvent and in the aqueous liquid at equilibrium) is desirably at least 10:1 and preferably as high as possible. It must be also chemically inert with respect
30 to the carrier.

The carriers are those having an internal porosity (or grain porosity) of at least 0.1, for example from 0.1 to 0.8. The internal porosity is defined as the ratio of the internal
35 free space to the real volume of the solid particles; it is measured for example by means of a mercury porosimeter. The internal porosity is thus different from the bed porosity, which is defined as the ratio be-
40 tween the intergranular free space and the apparent volume of the bed of particles.

This porosity enables the carrier to be impregnated with a liquid which remains immobilized and confined in its pores.

45 The carrier does not need to possess, by itself, any selectivity with respect to the compound to be extracted: it suffices that its pore size be large enough to permit penetration of the compound to be extracted, of the
50 extraction solvent and of the regeneration liquid.

Good results have been obtained with carriers comprising, for example, pumice, kieselguhr, bauxite, alumina, carbon (e.g.
55 coal), or silicates, in which a substantial volume of organic material can be immobilized in an apparently small volume. These materials may be used in the form of powder, granules, balls or extrudates of various
60 shapes. The size of the grains is preferably selected in the range 0.1 mm to 5 cm.

The preferred carriers are those which are substantially inert with respect to water, to the solvent and to the organic material, par-
65 ticularly those which do not swell appreci-

ably in contact with these materials. Inorganic carriers generally fulfil these conditions. For impregnating the porous carrier, there is selected a solvent having the properties already mentioned and convenient for
70 the considered case.

By way of example, when an aromatic hydrocarbon is to be extracted, there can be used advantageously, as immobilized liquid, a saturated paraffinic or cycloparaffinic hyd-
75 rocarbon or a mixture of these hydrocarbons, piquid at the extraction temperature, particularly those containing from 4 to 16 carbon atoms, particularly pentane hexane, isohexane, heptane, isooctane, decane, cyc-
80 lohexane or methylcyclopentane.

The amount of solvent used depends on the internal porosity of the porous material and on the porosity of the bed of this material. It may reach for example, from 20 to
85 75% by volume of the apparent filling volume. It has been moreover observed that, when the organic material content of the recovered effluent reaches a value predetermined as the maximum acceptable
90 value, the extraction mass can be regenerated by contacting it with the same solvent as used for the impregnation, or with a different solvent complying nevertheless with the above-mentioned conditions.
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Thus the extraction mass can effectively be washed, during which the solvent at least partly replaces the previously-absorbed organic material.

Other conventional regeneration methods
100 may be used. For example, it is possible to evaporate the liquids by subjecting the mass to reduced pressure or to stripping. It is however preferred to proceed by re-extraction, so that the extraction mass can
105 be immediately re-used without further power consumption.

According to one embodiment of the invention, the grains of the porous carrier, preliminarily dried, and placed for example
110 in a column, are impregnated before use with a conveniently selected solvent which fills the pores of the carrier. The solvent in excess is allowed to flow out to the maximum extent. Then water is passed through
115 the grains of the so-impregnated carrier. If so desired, the first obtained water fraction, which contains solvent carried away from the intergranular space of the carrier, is removed.
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When it is observed that the impregnated carrier is nearly fully saturated i.e. when the extraction rate falls below a selected limit control value, regeneration is performed as above-indicated. The amount of solvent
125 required for the regeneration has been found in practice not very large.

At the end of the regeneration step, there is obtained a solution of the organic compound in the regeneration solvent. This mix-
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ture can be fractionated. However, when by reason of the nature of the solvent and the extracted material, such a fractionation would be too difficult, or for any other reason, the absorption mass can if desired be regenerated with another solvent than that used for the initial impregnation. For example, a carrier initially impregnated with octane and on which there has been absorbed, for example, ethylbenzene, can be regenerated with pentane.

Another preferred embodiment consists of using at least two columns, preferably three columns, one or preferably two of which are used to perform the extraction step, in order to use the carrier capacity to the largest possible extent, while the remaining column is under regeneration. Successive columns of the group can in this way be regenerated in sequence.

A fixed bed of particles of the impregnated carrier can be used efficiently for the absorption step, with flow rates of aqueous liquid to be purified, for example, in the range 100 cc/cm²/h to 5000 cc/cm²/h, preferably from 500 cc/cm²/h to 2000 cc/cm²/h (cc/cm²/h means a volume of liquid per unit section of the bed and per hour). An advantageous ratio of the amount of water to be treated to the amount of impregnated porous carrier is from 1:1 to 5000:1, preferably from 100:1 to 2000:1.

During regeneration, the solvent flow rate can be, for example, from 10 to 500 cc/cm²/h.

The above-mentioned flow rates are average values and can be modified to a large extent in accordance with the particular operating conditions of the process.

Examples of organic compounds easily extractable from aqueous effluents are liquid aromatic hydrocarbons containing from 6 to 20 carbon atoms, for example benzene, toluene, xylenes, styrene, ethylbenzene, dodecylbenzene; chlorinated and fluorinated liquid hydrocarbons, for example trichloroethylene, dichloroethane; vegetable or animal oils, for example fish oils, colza oil or palm oil; heavy liquid alcohols, heavy liquid ketones, heavy liquid amines, phenols, and liquid heterocyclic compounds such as thiophene or furan. "Heavy" compounds include compounds containing 8 or more carbon atoms per molecule.

These various compounds are present in small amounts in water, usually in a proportion of less than 5% by volume, more often less than 0.1% by weight. The minimum content depends on the efficiency of the extraction mass and of the rulings in force concerning the dishcharge of polluted waters. In some cases, aqueous liquids containing 10–1000 parts per million (by weight) of organic compounds or even less, can be treated by the process of the invention.

The following examples illustrate the invention without however limiting the scope thereof.

EXAMPLE 1

A column having an internal diameter of 0.8 cm is filled, up to a height of 36 cm, with granulated pumice having a particle size from 0.08 cm to 0.1 cm. The weight of dried pumice is 7.5 g, the porosity of the resulting bed is 0.4 and the grain porosity 0.53.

A stream of isooctane, fed through the lower end of the column, is passed therethrough until the air bubbles have disappeared in pumice and the liquid in excess is allowed to drip. Then, an aqueous solution containing 60 ppm by weight of ethylbenzene (ppm = part per million of parts) is passed through the column.

The first obtained fraction, i.e. about 20 cc, is removed and the recovered water is analysed. It is observed that ethylbenzene is not detectable until 4,500 cc of polluted water have been passed through the column. At that time, the recovered water contains 5 ppm by weight of ethylbenzene.

The operation is discontinued and desorption is performed by passing isooctane downwardly through the column at a flow rate of 12 cc/h. 75cc of isooctane are required for desorbing 99.5% of the ethylbenzene retained in the impregnated pumice.

Polluted water is again passed through the column under the same conditions. The amount of recovered water containing less than 5 ppm by weight of ethylbenzene remains substantially the same.

EXAMPLE 2 (comparison)

Example 1 is repeated but with dry pumice, not impregnated with isooctane. It is observed that the ethylbenzene content of the recovered effluent reaches 10 ppm by weight after passage of 0.2 liter of water polluted with 60 ppm of ethylbenzene, idential to that of example 1.

EXAMPLE 3

The same column as in example 1 is used but the pumice is impregnated with pentane. 600 cc/h of an aqueous solution containing 60 ppm by weight of styrene is passed through the column. After passage of 3000 cc of polluted water, it is observed that the styrene content of the recovered effluent reaches 5 ppm by weight.

Regeneration is achieved by passing 110 cc of pentane through the column at a rate of 12 cc/h. There is thus desorbed 99.8% of the absorbed styrene. Pentane and styrene can be separated by distillation.

EXAMPLE 4

The same column as in example 1 is used, but the porous solid consists of kieselguhr particles. The weight of dry carrier is 9.5 g. The bed porosity is 0.21 and the grain poros-

ity 0.75.

The column is impregnated with pentane and there is percolated therethrough water containing 60 ppm of styrene, at a flow rate of 300 cc/h. The styrene content of the effluent reaches 5 ppm after passage of 4,000 cc of water. The desorption performed with pentane percolated at a flow rate of 30 cc/h results in the recovering of 99.6% of the absorbed styrene after passage of 150 cc of pentane.

EXAMPLE 5

The same column as in example 1 is used; the filling material consists of pumice grains of a diameter from 0.01 to 0.03 cm; the impregnation solvent is pentane. An aqueous solution with a 60 ppm by weight content of benzene is passed therethrough at a flow rate of 300 cc/h. There is obtained an effluent free of benzene content amounts to 5 ppm. The desorption is performed with 15 cc of pentane used at a rate of 30 cc per hour. The absorption operation can then be resumed.

EXAMPLE 6

There is used a cylindrical column one meter high and having a capacity of 195 cc, filled up with active carbon grains of a diameter from 0.08 cm to 0.10 cm. The carbon weight is 74.5 g, the bed porosity is 0.41 and the grain porosity 0.68.

The impregnation of the active carbon is performed by passing a steam of pentane through the column. The liquid in excess is then allowed to flow out by gravity. An aqueous solution containing 60 ppm by weight of benzene is passed through said column at a flow rate of 1,800 cc/h; the effluent does not contain any detectable amount of benzene until 40 liters of water have been passed through the column. At that time a benzene content of 5 ppm is observed. The regeneration of the column is performed by passing n-pentane therethrough at a rate of 30 cc/h; after passage of 500 cc of pentane 99.5% of the absorbed benzene has been recovered.

The test can be reproduced under the same conditions and gives a similar result.

EXAMPLE 7

The operating conditions are the same as hereabove except that the benzene solution is replaced with an aqueous solution of ethylbenzene at a concentration of 130 ppm by weight; the effluent water is pure up to the passage of 270 liters. The desorption is performed with pentane at a rate of 60 cc/h; after passage of 1,500 cc of pentane, 99.5% of the absorbed ethylbenzene has been removed.

EXAMPLE 8

A cylindrical column of 40 cm height and of a 2 cm diameter is filled up with pumice grains of a diameter ranging from 0.025 to 0.1 cm; the carrier is impregnated with octanol. The treated fluid consists of an aqueous solution containing 20 ppm by weight of phenol; it passes at a rate of 600 cc/h. The presence of phenol in the effluent is observed after passage of 500 cc of solution. The regeneration of the column is performed by passage of 50 cc of octanol at a rate of 60 cc/h.

WHAT WE CLAIM IS:-

1. A process for extracting an organic compound from an aqueous liquid containing it, that comprises contacting the aqueous liquid containing the organic compound with an extraction mass comprising particles of an inert porous solid carrier having a grain porosity of at least 0.1 and containing an immobilized organic solvent, with substantially no organic solvent in the space between the particles, said solvent being a good solvent for the organic compound to be extracted and having low solubility in the aqueous liquid, said organic solvent and porous carrier being such that the solvent is chemically inert with respect to the carrier and has substantially no swelling effect on the carrier; the process also comprising regenerating the extraction mass after said contact by contacting it with an organic solvent as hereinabove defined.

2. A process according to claim 1, in which the solubility of the organic solvent in the aqueous liquid is lower than that of the organic compound in the same aqueous liquid.

3. A process according to claim 1 or 2, in which the solvent used for the regeneration step is identical to that initially present in the porous carrier.

4. A process according to claim 2 or 3, in which the solubility of the solvent in the aqueous liquid is lower than 0.1% by weight, and the distribution coefficient of the organic compound between the solvent and the aqueous liquid is at least 10:1.

5. A process according to claim 3, in which the solubility of the solvent in the aqueous liquid is lower than 0.01% by weight.

6. A process according to any preceding claim, in which the porous carrier is an inert inorganic carrier having an internal porosity of at least 0.1.

7. A process according to claim 6, in which the carrier comprises pumice, alumina, bauxite, kieselguhr, carbon or a silicate.

8. A process according to any preceding claim, in which the organic compound to be extracted comprises at least one aromatic hydrocarbon and the solvent comprises at least one saturated hydrocarbon which is liquid at the extraction temperature.

9. A process according to claim 8, in which the organic compound to be extracted comprises styrene or ethylbenzene.

10. A process according to any preced-

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ing claim, in which the amounts of aqueous liquid to be treated and of impregnated carrier are in a ratio by weight in the range 1:1 to 5000:1.

11. A process according to any preceding claim, in which the particles of the extraction mass are arranged in a fixed bed and the hourly flow rate of the aqueous liquid passing through said bed is from 100 to 5000 cc per cm² of bed section.

12. A process according to any preceding claim, in which the organic compound content of the aqueous liquid is lower than 5% by volume.

13. A process according to claim 12, in which the organic compound content of the aqueous liquid is from 10 to 1000 parts per million (by weight).

14. A process according to any preced-

ing claim, in which the carrier is not selective with respect to the compound to be extracted.

15. A process according to any preceding claim, in which the solubility of the solvent in the aqueous liquid is at least three times lower than that of the organic compound in the same aqueous liquid.

16. A process for extracting organic compounds from an aqueous liquid, substantially as hereinbefore described with reference to any one of Examples 1 and 3–8.

17. An aqueous liquid purified by a process according to any preceding claim.

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